Comments on **Biogeosciences Discuss., 2014-354**: "Processes determining the marine alkalinity and carbonate saturation distributions" by **B. R. Carter** et al.

I. General comments

In this manuscript, the authors introduce a composite tracer Alk* to study the process determining the marine alkalinity and calcium carbonate saturation distributions. The authors present the global distributions of Alk* and estimate the riverine A_T budget for different ocean basins. On regional scale, the authors highlight the high Alk* near river mouths due to riverine input and low Alk* in the Red Sea due to biological precipitation of $CaCO_3$. For the variability of carbonate saturation state, the authors define a metric to evaluate the importance of various controlling factors. Overall, the subject of this manuscript meets the general interest of Biogeosciences and I support the publication of this work after a moderate modification. Please see below for my detailed comments.

II. Specific comments

1. p11141, line 18-21: "The marine A_T distribution is affected by the cycling of carbonate, freshwater, and organic matter, so we develop the quasi-conservative tracer Alk* to isolate the influences carbonate cycling."

Variations of alkalinity in the ocean are mainly controlled by the following processes: 1) mixing between different water masses, (2) precipitation and evaporation, (3) production and remineralization of organic matter, (4) precipitation and dissolution of $CaCO_3$, (5) external sources such as riverine input, underground water, hydrothermal vent fluids, (6) redox reactions in anaerobic environment [*Chen*, 2002]. By integrating the concept of potential alkalinity, the tracer Alk* is not affected by production and remineralization of organic matter (process 3). In addition, the influence of precipitation and evaporation (process 2) is removed by using the salinity-normalization method of Robbins (2001). On general, Alk* is primarily affected by mixing (process 1), precipitation and dissolution of $CaCO_3$ (process 4), riverine input (process 5). However, it should be mentioned that, in some special marine environments, the contributions of hydrothermal vent fluids, and redox reactions may be significant. In these cases, Alk* is no longer a good "tracer to isolate the influences of carbonate cycling".

2. p11142, lines 7-19.

Please revise these sentences for a more accurate description of nitrogen cycle and its influence on alkalinity.

The three reaction equations here are questionable (e.g., nitrification starts from NH_3 or NH_4^+ in R1, R2 gives unrealistic product O_2 in denitrification). These equations are not really useful for the following discussion and I suggest to remove them. If the authors want to keep these equations, please refer to the equations by *Wolf-Gladrow et al.* [2007].

3. p11144, Eqs. 3-5

The global mean passive conservative potential alkalinity (A_P^C) is subtracted from potential alkalinity (A_P) to calculate Alk* (Eqs. 3-5). Instead of using the global mean A_P^C, is it better to use the mean surface A_P^C in the low-latitude tropical open oceans? In these oligotrophic waters, influences of riverine input, convection and biogenic $CaCO_3$ production are minor while most of alkalinity variability is controlled by precipitation and evaporation [*Jiang et al.*, 2014; *Millero et al.*, 1998]. Therefore, it provides a better reference for defining Alk*. In this way, positive Alk* indicates alkalinity inputs (riverine inputs, upwelled deep water et al.) while negative Alk* suggests alkalinity removal ($CaCO_3$ precipitation et al.).

4. p11144, lines 14-24.

The authors discuss the difference between Alk* and the typical salinity-normalized result (sA_P). The reasons why "sA_P does not mix conservatively, has a variable response to carbonate production, and yields an undefined value for a riverine end-member with zero salinity and non-zero A_P" and "the non-linearity of sA_P" are discussed in detailed by *Jiang et al.* [2014].

5. p11145- 11146, section 3.1

This section is not well-organized and Figs. 2-5 need more explanations. Consider to discuss the surface distribution (Fig. 2&3) in one paragraph and discuss the vertical gradient (Fig. 4&5) in the second paragraph.

6. "The similarity between phosphate and Alk* distributions suggests that Alk* captures the portion of A_T that varies in response to biological cycling as the hard parts of marine organisms." p11145, lines 23-24

This statement is not really true and need more explanations. Although the surface ocean Alk* and phosphate have the same sources (upwelled deep water enriched in Alk* and nutrient, riverine inputs), they are removed by different biological activities. Production of particle organic carbon (POC) decreases phosphate but has no effect on changing Alk*. In contrast, precipitation of $CaCO_3$ decreases Alk* without changing phosphate. As a result, the low surface concentrations of phosphate and Alk* in the low-latitude open ocean are due to the weak convention and low biological productions of POC and $CaCO_3$. The high concentrations of phosphate and Alk* are generally in the high-nutrient low-chlorophyll (HNLC) regions, which is mainly due to the strong convention and low productions of POC and $CaCO_3$. On the other hand, the surface concentrations of phosphate and Alk* are related to the ratio of $CaCO_3$/POC production (the rain ratio). Given the same initial condition, high rain ratio would result in relatively low Alk* and high phosphate, and vice versa.

7. Section 3.3:

Although the Amazon is the largest A_T source, its Alk* is relatively low. Therefore, the Amazon is not the best example to show the riverine Alk*. I don't find Fig. 7 and the discussion on winter-summer difference (p11148, line 19 - p11149, line 2) are

closed related to the main objectives of this study.

The third paragraph (p11149, lines 15-30) only presents the estimates of the rivrine Alk*. It should be moved to section 3.2 (constructing the riverine A_T budget for ocean basins) or moved to supplement.

8. The authors define surface ocean as the top 50m of water column. It seems that 50m is a little bit deep. Normally, it is 20m depth in the (sub)tropics and 30m depth at high latitudes [*Lee et al.*, 2006]. Meanwhile, the boundary between the Atlantic and the Arctic defined by the authors (40° N) seems a little bit south?

9. Section 4.2, p11153, lines 13-25:
$\Omega=[Ca^{2+}]\,[CO_3^{--}]\,/\,K'_{sp}$, any factor affecting $[Ca^{2+}]$, $[CO_3^{--}]$, or K'_{sp} can modulate Ω. Why only C_T is mentioned in the discussions here?

10. Conclusions:
This section is too long. Please provide more concise conclusions.

III. Technical corrections
"carbonate saturation" => calcium carbonate saturation throughout the manuscript.

p11140, line 20:
"to isolate the influences carbonate" => to isolate the influences of carbonate

p11142, line 5:
"while still mixing" => while still mixing conservatively

p11145, lines 21-22:
"The similarity of the A_T and salinity distributions demonstrates the strong influence of freshwater cycling on the surface marine A_T distribution [*Jiang et al.*, 2014; *Millero et al.*, 1998]". Please add references here.

p11146, line 1-2
"The Alk* distribution has a broadly similar explanation to the phosphate distribution." is a repetitive sentence. Delete it.

p11149, line 27:
"into the Yellow Sea" => into the East China Sea

p11152, line 21:
"alongside the ... values". Please correct the symbols in this sentence.

p11154, lines 17-18:
"A plot of Alk* against salinity reveals the large A_T input from the Amazon River". This sentence come from nowhere (which plot?).

Fig. 6:
The color (the numbers of measurements) in this figure is not really useful.

References:

Chen, C.-T. A. (2002), Shelf-vs. dissolution-generated alkalinity above the chemical lysocline, *Deep Sea Research Part II: Topical Studies in Oceanography, 49*(24–25), 5365-5375, doi: 10.1016/S0967-0645(02)00196-0.

Jiang, Z.-P., T. Tyrrell, D. J. Hydes, M. Dai, and S. Hartman (2014), Variability of alkalinity and alkalinity-salinity relationship in the tropical and subtropical surface ocean, *Global Biogeochemical Cycles*, *28*, 729-742.

Lee, K., L. T. Tong, F. J. Millero, C. L. Sabine, A. G. Dickson, C. Goyet, G. H. Park, R. Wanninkhof, R. A. Feely, and R. M. Key (2006), Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophysical Research Letters, 33*(19), L19605, doi: 10.1029/2006gl027207.

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Wolf-Gladrow, D. A., R. E. Zeebe, C. Klaas, A. Kortzinger, and A. G. Dickson (2007), Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, *Marine Chemistry, 106*(1-2), 287-300, doi: 10.1016/j.marchem.2007.01.006.